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NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER
Bethesda, Md. 20034

BIOLOGICALLY ACTIVE POLYMERIC COATING MATERIALS

by

E. J. Dyckman, J. A. Montemarano,
and D. E. Gilbert

MATERIALS DEPARTMENT
Annapolis
RESEARCH AND DEVELOPMENT REPORT

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18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

organometallic polyacrylates, polyvinyls, polyesters, epoxies, polyurethanes, accelerated aging trials, leaching rate, antifouling, antifouling coatings

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Over 100 organometallic polyacrylates, polyvinyls, polyesters, epoxies, and polyurethanes have been synthesized and are undergoing antifouling performance evaluation in Pearl Harbor, Hawaii, and Miami Beach, Florida. During accelerated aging trials, using a rotating cylinder apparatus, organometallic polymers have demonstrated from 1/2 to 1/15 the leaching rate of a Navy (over)

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20. ABSTRACT
(Cont)
experimental antifouling coating, formula 1020A. The same
organometallic polymers continue to exhibit 100% antifouling
effectiveness after up to a 2 1/2-year exposure in the severe
fouling climate of Pearl Harbor, Hawaii. Four organometallic
polymers have been selected for use in the formulation of
experimental antifouling coatings with air-pollution-exempt
solvents. Two experimental formulations using one organo-
metallic polymer have been completed and are undergoing panel
immersion trials at Pearl Harbor, Hawaii, and Miami Beach,
Florida. Acute mammalian toxicity studies of this organometallic
polymer have been completed, as well as recommendations for
its safe handling by shipyard personnel.

(Authors)

ADMINISTRATIVE INFORMATION

This work is authorized under Program Element 62755N, Task Area SF 53 554 706, Task 16472, Work Unit 2853-102, as described in the 1 May 1974 Program Summary.

LIST OF ABBREVIATIONS

$^\circ$ C	- degrees Centigrade
cm^2	- square centimeters
gm	- gram
ID	- inside diameter
LR	- leaching rate
MEKP	- methyl ethyl ketone peroxide
μg	- microgram
ml	- milliliter
OD	- outside diameter
OMP	- organometallic polymer
pph	- parts per hundred
TDI	- toluene di-isocynate
TETA	- triethylenetetramine

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INTRODUCTION

Organometallic polymers exhibiting minimal pollution hazard and maximum antifouling effectiveness are being developed as antifouling coating materials for ships and submarines to meet Navy objectives. One such objective requires the use of antifouling coatings that meet expected Environmental Protection Agency regulations limiting discharge of antifouling pesticides into the marine and freshwater environment. Another strategic objective requires that ship and submarine hulls remain free from marine growth for at least 5 to 6 years, as opposed to the 1- to 3-year longevity exhibited by present in-service antifouling coatings. The use of long-lived antifouling coatings would extend the interval between dry docking of ships and submarines to 5 years without risking interruption, due to hull fouling of their performance of basic missions, as presently experienced. Also, an economic objective suggests the use of low-leaching/long-lived antifouling materials for additional applications where fouling and biodeterioration of structures have resulted in frequent high cost maintenance operations; e.g., pilings, for which a 25-year service life is required, but on which present treatments fail in less than 10 years in tropical waters. This results in an estimated $200 million expenditure for piling replacement each year. In addition, current figures show that the Navy spends between $15 and $20 million per year for antifouling paint (exclusive of labor and drydock costs) in order to provide antifouling protection. Premature failure of present antifouling paints results in significant increases in ships' fuel consumption due to increased hull drag. Considering the current drydocking cycle of Navy ships (54-60 months between overhaul), this loss in fuel economy approaches $140 million, annually and Fleet-wide, in additional fuel costs.

Acceptable compliance with the above ecological, strategic, and economic objectives is well beyond the scope of present antifouling coating technology. Protective coatings currently in service consist of inorganic copper and organometallic salts in a finely divided form distributed throughout a coating binder. It has been the art of the formulator to select binder and sufficient toxicant to discourage or "poison" the fouling organisms during their early stages and, thereby, prevent firm attachment and growth to underwater surfaces, e.g., ships' hulls. Furthermore, state-of-the-art antifouling ship bottom coatings, which contain extremely high concentrations of antifouling agents, exhibit poorly controlled release rates and are generally depleted of their antifouling efficacy within their

first year of service.[1] This inefficiency leads to excessive amounts of metal contamination in the marine and freshwater environments, as well as to inadequate service life of the antifouling coatings.

The Center has been active in developing another concept for antifouling coatings - the use of biocidal binders.[2,3] In this work, organometallic polymeric films have been so designed that they are inherently poisonous to fouling organisms. As a result of this effort, it is now possible to reduce the ecological impact and extend the service life of antifouling coatings by means of polymerization of toxicant into paint resins. The coating binder is so constructed that the loss of toxicant by chemical disengagement from the binder results in the solution of the layers of the binder or, if the toxicant is able to migrate to the surface, the extraction rate of the toxicant can be minimized and remain nearly constant. This optimizes the efficiency of the coating system and reduces the amount of antifoulant necessary for long-term effectiveness, as compared to conventional paint systems.

MATERIALS AND METHODS

The synthesis of the organometallic polymers being tested for their antifouling performance is summarized in appendix A.

Experimental organometallic polymers were coated on Plexiglas and fiber glass panels (10 x 12 x 1/8 inch). Panel surfaces were roughened with emery paper, detergent washed, and thoroughly rinsed with deionized, distilled water. Two coats of the film-forming organometallic polymers were brushed onto the test surfaces, after which the panels were dried at room temperature for at least 1 week. Bulk polymerized organometallic polymers were primed with an adhesive and attached to Plexiglas panels. Antifouling paints, used as controls, were similarly brushed onto Plexiglas panels with a proper tie coat when necessary. At Pearl Harbor, Hawaii, and Miami Beach, Florida, test panels were immersed in 4 feet of water and photographed approximately every 4 months.

The relative rate of leaching of nine organometallic polymers and one tri-n-butyltin oxide/tri-n-butyltin fluoride-based antifouling coating (Navy formula 1020A) was determined. In an attempt to simulate shipboard trials, an accelerated aging device, the rotating cylinder apparatus, was used in comparing the tin release rate from each of the materials.

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[1]Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

4526   2

Plexiglas cylinders (3 1/4-inch OD[x] x 10 inches long) were roughened with emery paper, detergent washed, and thoroughly rinsed with deionized, distilled water. Two coats of the organometallic polymer or the antifouling paint were brushed onto the cylinders; the cylinders were then dried at room temperature for at least 1 week. The rotating cylinder apparatus consisted of a 60-gallon capacity glass tank, through which filtered Chesapeake Bay water flowed continuously. The coated cylinders rotated at an equivalent surface speed of 1.85 knots in this tank. Each cylinder was suspended vertically in the tank by an aluminum shaft driven by a variable-speed, high-torque, electric motor. The cylinders, totally immersed in the flowing water, rotated continuously, all in the same direction.

Each week, the cylinders were simultaneously removed from the tank and were transferred wet, wiped with soft paper toweling, and placed in separate Pyrex glass battery jars (5 3/4-inch ID x 12 inches high) filled with filtered Chesapeake Bay water for measuring the leaching rate. All cylinders were tested in the rotating mode for a standard amount of time. While the cylinders continued to revolve at 1.85 knots in the battery jars, 25-ml aliquots of the water were analyzed for tin content with a Perkin Elmer, model 303, atomic absorption spectrophotometer. After sampling, the cylinders were then returned, wet, to the 60-gallon tank.

After each analysis, the battery jars were cleaned with H_2SO_4-$NaCrO_4$ solution and thoroughly rinsed with distilled water. In the calculation of the leaching rate, if the exposed area of the coating was "x" cm^2, and the amount of tin released in 120 minutes was "y" µg, the leaching rate amounts to: $(12y/x)$ µg $Sn/cm^2/day$.

RESULTS AND DISCUSSION

Organometallic polyacrylates, polyvinyls, polyesters, epoxies, and polyurethanes were prepared. These polymers were synthesized either by copolymerizing organometallic monomers with vinyl monomers and/or unsaturated alkyds, or through a condensation reaction of an organometallic oxide and a resin containing carboxylic acid groups as side chains. The various organometallic polymers synthesized differ with respect to

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[x]A list of abbreviations used in this text appears on page i.

polymer type, molecular weight, substitution of moieties along the polymer backbone, and degree of crosslinking within the polymer backbone.

Patch panel trials for the evaluation of the antifouling performance of organometallic polymers were conducted at NAVSHIPYD PEARL and at Miami Beach, Florida. After a 2 1/2 year exposure, several OMPs continued to exhibit excellent anti-fouling performance, including M1 (CP1, figure 1), P43 (figure 2), P37 (figure 3), and P13 (figure 4). Exposure data (appendix B) also indicated that good antifouling performance may be expected from styrene (S6) and polyester (P54, figure 5) organometallic resins. To date, the antifouling performance of epoxy (WS 52B, figure 6) and polyurethane organometallic resins have shown good antifouling performance after a few months of immersion. Similarly, copolymers based on organolead monomers and hydroxy-alkylacrylates have just commenced immersion and antifouling performance. Data are not yet available for these polymers.

As previously reported, several OMPs have been selected for formulation into experimental Navy antifouling coatings. One organometallic polymer, OMP 1, has been used to formulate two experimental antifouling coatings with an air-pollution-exempt solvent. Test panels coated with these OMP formulations, with Navy formula 1020A (based on tri-n-butyltin oxide and tri-n-butyltin fluoride) and with Navy Formula 121/63 (based on cuprous oxide) are undergoing exposure at NAVSHIPYD PEARL and Miami Beach, Florida, to compare their antifouling performance.

Before OMPs can be used in Navy antifouling coating formulations, acute and chronic mammalian toxicity studies need to be performed on each OMP. Acute mammalian toxicity studies for OMP 1 have been completed.[4]

The influence of chemical parameters on leaching rate, such as polymer type, molecular weight, substitution of moieties along the polymer backbone, and degree of crosslinking within the polymer backbone, was studied. The relative LR of the OMPs (shown in table 1) and formula 1020A was determined with the rotating cylinder apparatus. After the OMPs and formula 1020A were aged for 28 days in Chesapeake Bay water, leaching rate data (figure 7) indicated that chemical parameters influenced the rate of release of antifouling moieties. Furthermore, they indicated that there is no apparent relationship between LR of organotin from the antifouling coating materials tested and their respective percentages of tin content.

TABLE 1

ORGANOMETALLIC POLYMERS TESTED FOR LEACHING RATE

OMP	Other Designation	Description
1	M1	Poly (tri-n-butyltin methacrylate/ tri-n-propyltin methacrylate/ methyl methacrylate)
2	P43	Poly (tri-n-butyltin methacrylate/ methyl methacrylate)
4a	P36	Tri-n-butyltin ester of low molecular weight poly (methyl vinyl ether/ maleic acid)
4b	P37	Tri-n-butyltin ester of high molecular weight poly (methyl vinyl ether/maleic acid)
4c	P65	Tri-n-butyltin ester of poly (methyl vinyl ether/ethyl maleate/maleic acid)
5a	P13	Tri-n-butyltin ester of crosslinked polymethacrylic acid (63% by weight), Union Carbide VAGH resin (22%), and Westvacco WW rosin (15%)
5b		Tri-n-butyltin ester of crosslinked polymethacrylic acid (61% by weight) and Monsanto C5V16 resin (39%)
6	P80	Unsaturated polyester resin Hetron 22992 crosslinked by tri-n-butyltin methacrylate
7	P108	Poly (glycidyl methacrylate/tri-n-butyltin methacrylate) cured by 1,8-methanediamine

In comparing the relative LR of polymerized organometallic compounds with an organometallic salt-based antifouling coating (table 2), it is apparent that, in all cases but one, the LR of OMPs is less than that of formula 1020A. Figure 7 and table 2 show that the polymer type exhibiting the lowest rate is vinylic (OMPs 4a and 4b). In comparing the LR of the polyvinyls, OMPs 4a and 4b, it is apparent that the higher the molecular weight of the polymer, the lower the LR. Similarly, comparing polymethacrylates, OMPs 5a and 2, the polymer with the greater degree of crosslinking within the polymer backbone had the lower LR. Finally, substitution of moieties within the poly-vinyls influences their relative LR. When half the tri-n-butyltin moieties contained in OMPs 4a and 4b were replaced by ethyl moieties in OMP 4c, data indicated that the presence of ethyl substituents accelerated the hydrolysis of organotin moieties (from OMP 4c by a factor of 10 to 15 over that of OMPs 4a and 4b). Therefore, the effects of substituents along the polymer backbone also seem to affect the LR of organo-metallic polymers.

TABLE 2 - RELATIVE RATE OF LEACHING OF ORGANOMETALLIC POLYMERS AS COMPARED TO 1020A

Antifouling Coating Material	% Tin by weight	LR* μg tin/cm^2/day	$\dfrac{LR_{OMP}}{LR_{1020A}}$
1020A	20.2	79.4	1.00
OMP 1	29.3	35.7	0.45
OMP 2	25.0	11.3	0.14
OMP 4a	32.5	7.6	0.10
OMP 4b	32.5	5.8	0.07
OMP 4c	24.3	85.6	1.08
OMP 5a	19.9	8.7	0.11
OMP 5b	19.3	11.3	0.14
OMP 6	4.8	9.5	0.12
OMP 7	22.4	18.2	0.23

*As determined utilizing rotating cylinder apparatus.

CONCLUSIONS

It has been concluded that:

● OMPs have lower leaching rates than Navy anti-fouling formula 1020A and exhibit long-term antifouling performance.

● OMPs can be formulated into experimental anti-fouling coatings by using air-pollution-exempt solvents.

● The leaching rate of OMPs is dependent on chemical parameters such as polymer type, molecular weight, substitution of moieties along the polymer backbone, and degree of cross linking within the polymer backbone.

● By means of chemical modification, the leaching rate of OMPs can be minimized while excellent antifouling performance is retained.

TECHNICAL REFERENCES

1 - Van Londen, A. M., "A Study of Shipbottom Paints in Particular Pertaining to the Behavior and Action of Anti-fouling Paints," Paint Research Inst., TNO Netherlands Research Center Rept 54C (Sep 1963)

2 - Dyckman, E. J., et al, "Nonpolluting Antifouling Organo-metallic Polymers," NSRDC Rept 3581 (Oct 1972)

3 - Dyckman, E. J., and J. A. Montemarano, "Antifouling Organometallic Polymers: Environmentally Compatible Materials," NSRDC Rept 4186 (Feb 1974)

4 - Miller, A. M., "Toxicity of Organometallic Antifouling Materials, Part I - Mammalian Toxicity of Organometallic Polymer OMP-1," NSRDC Rept MAT-74-54 (in publication)

Before   After
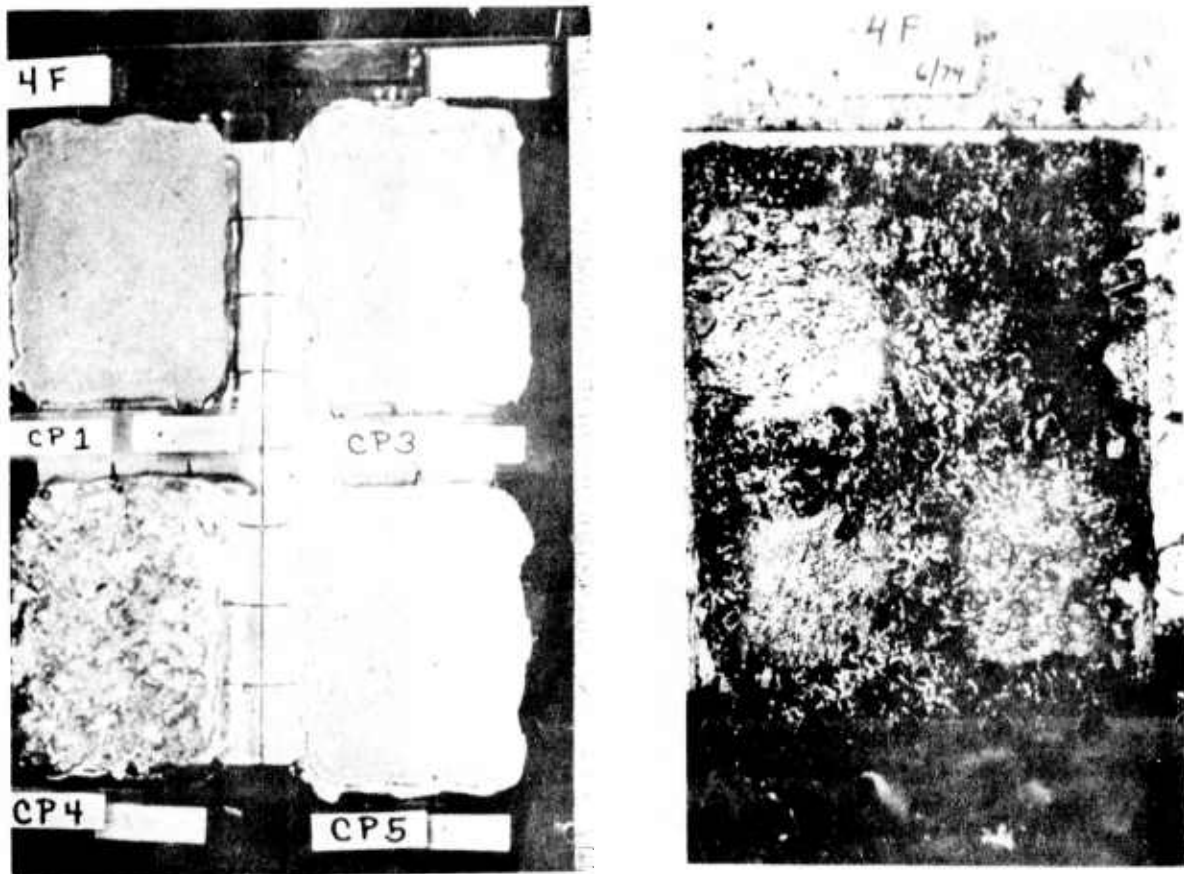
Figure 1
Fouling Resistance of Organometallic Polyacrylates
and Polyvinyls Before and After Exposure for
31 Months at NAVSHIPYD PEARL

4526
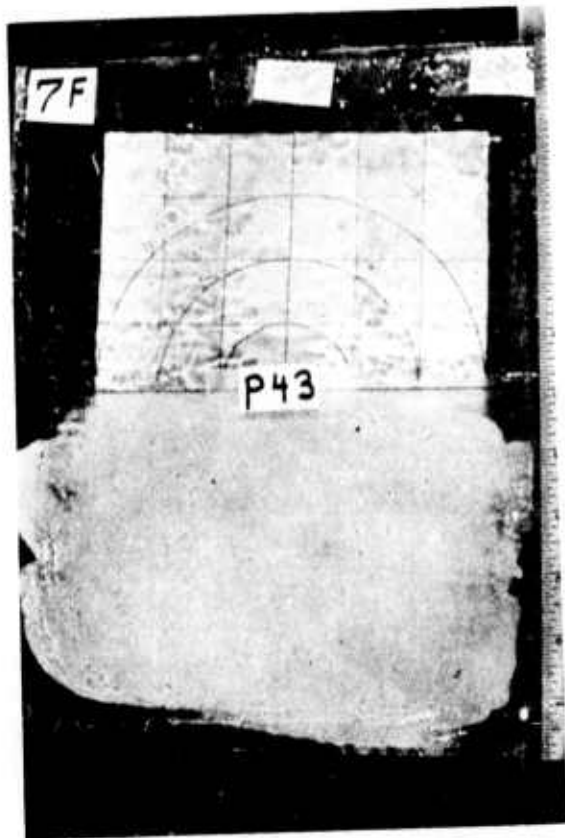
Before   After

Figure 2
Fouling Resistance of Organometallic Polymethacrylate
Before and After Exposure for
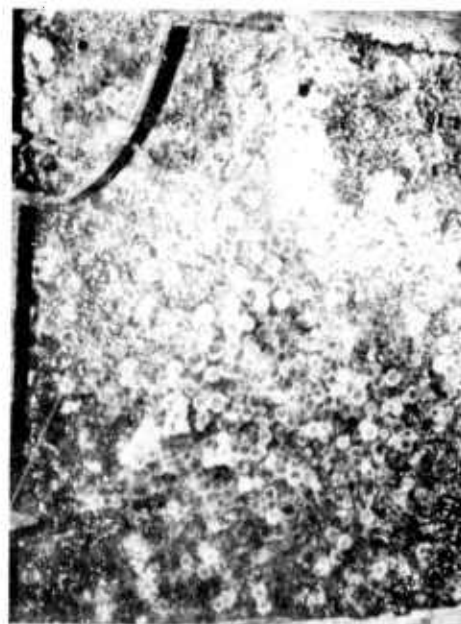29 Months at NAVSHIPYD PEARL

Before   After

Figure 3
Fouling Resistance of Organometallic Polyvinyls
Before and After Exposure for
29 Months at NAVSHIPYD PEARL
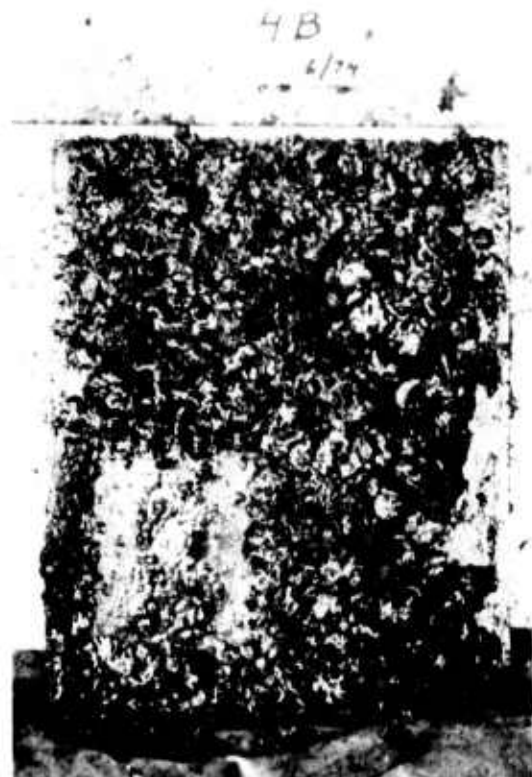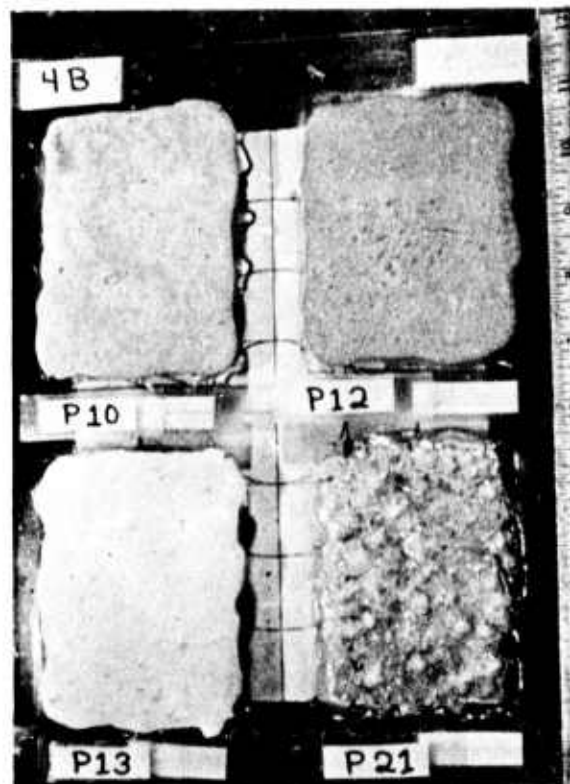
Before　　　　　　　　　　　　　　After

Figure 4
Fouling Resistance of
Organometallic Crosslinked Polymethacrylate
Before and After Exposure for
31 Months at NAVSHIPYD PEARL

4526

Before

P54
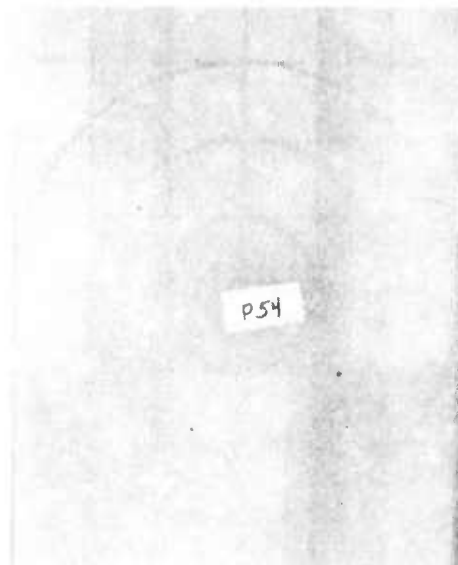
After, Pearl

After, Miami

21F
6/74

Figure 5 - Fouling Resistance of Organometallic Polyester
Before and After Exposure for 17 Months at NAVSHIPYD PEARL
and 15 Months at Miami Beach, Florida

4526
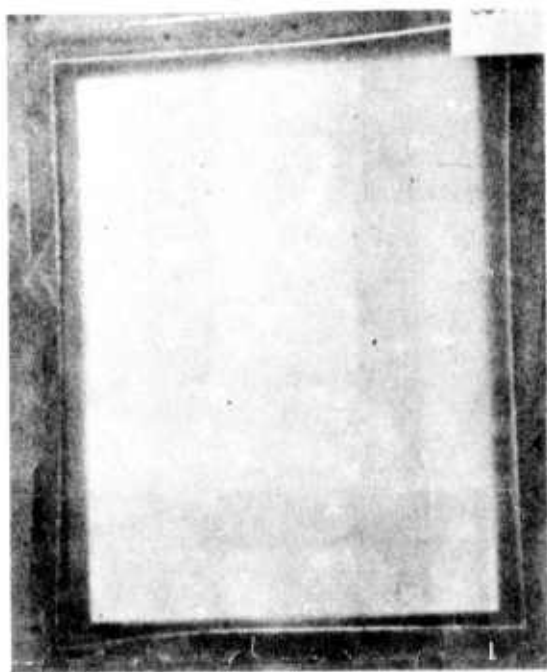
Before   After

Figure 6
Fouling Resistance of Organometallic Epoxy
Before and After Exposure for
7 Months at Miami Beach, Florida
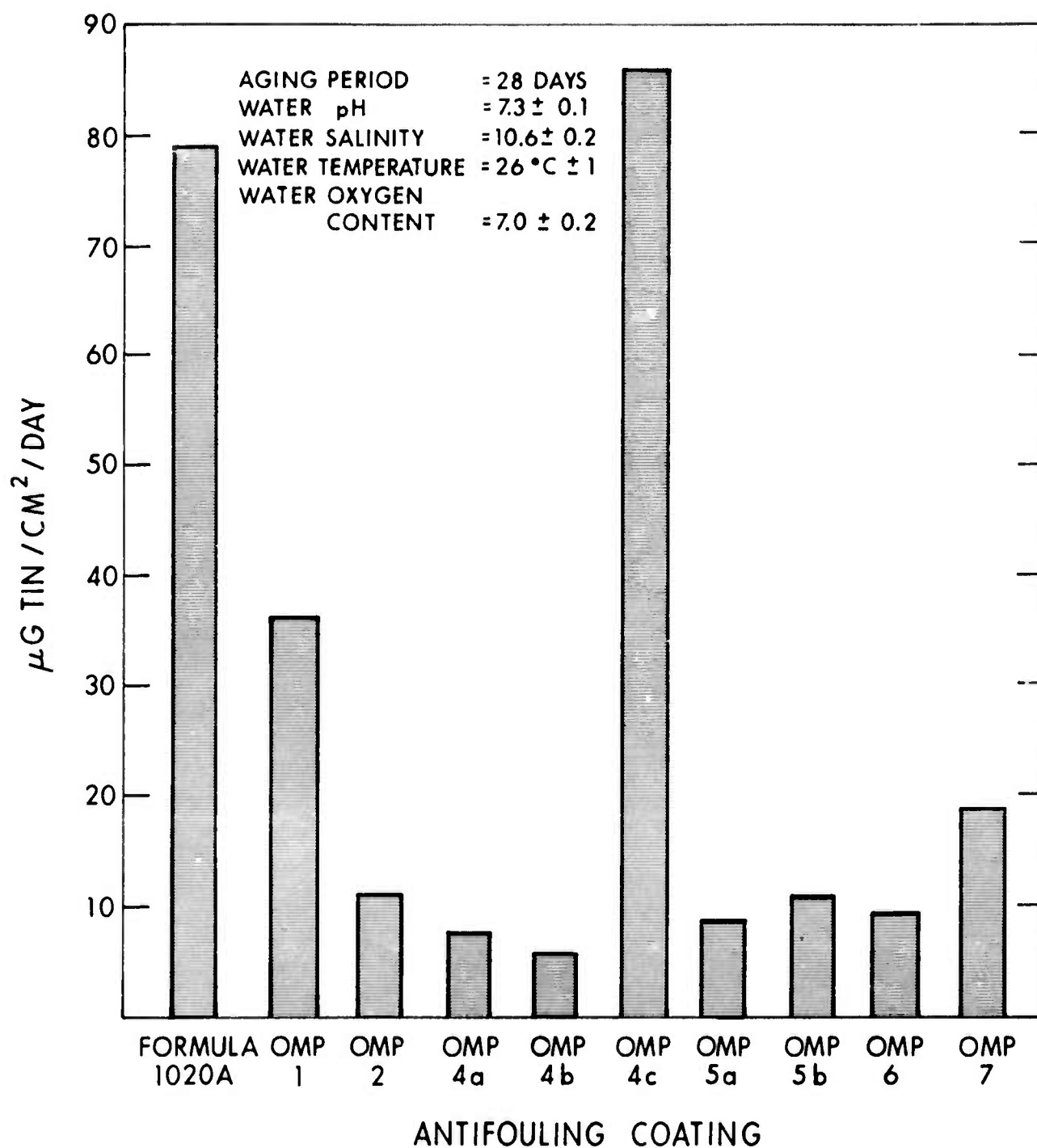
Figure 7
Rate of Leaching of Organotin from
Formula 1020A and Nine Organometallic Polymers

APPENDIX A
SYNTHESIS OF ORGANOMETALLIC POLYMERS

REFERENCES

(a) Dyckman, E. J., et al, "Nonpolluting Antifouling Polymers," NSRDC Rept 3581 (Nov 1972)

(b) Dyckman, E. J., and J. A. Montemarano, "Antifouling Organometallic Polymers: Environmentally Compatible Materials," NSRDC Rept 4186 (Feb 1974)

(c) Montermoso, J. C., et al, "Organotin Acrylic Polymers," U.S. Patent 3,016,360 (1962)

(d) Tech. Bulletin 425A, Emery Industries, Inc. (Jan 1970)

(e) Service Bulletin 2707, Hooker-Durez Division, Hooker Chemical Corp. (Sep 1968)

(f) Chemicals and Plastics Physical Properties, Union Carbide (1973-1974)

(g) Corredor, H., Unpublished Ph.D. Thesis, Washington State University, Pullman, Washington (1974)

The preparation of the following organometallic polymers is given in reference (a).

P2, Poly(tri-n-propyltin acrylate)

P5, Poly(tri-n-butyltin acrylate/tri-n-propyltin acrylate)

P13, Poly(tri-n-butyltin methacrylate)

P16, Poly(trimethyltin acrylate)

P17, Poly(trimethyltin methacrylate)

P20, Poly(tri-n-butyltin acrylate)

P21, Poly(trimethyltin acrylate)

P24, Poly(tribenzyltin acrylate)

P25, Poly(tri-n-propyltin acrylate)

P30, Poly(tri-n-butyltin methacrylate/methyl methacrylate)

P31, Poly(tri-n-propyltin methacrylate)

P34, Poly(tri-n-propyltin methacrylate)

P36, Tri-n-butyltin ester of poly(methyl vinyl ether/ maleic acid)

P37, Tri-n-butyltin ester of poly(methyl vinyl ether/ maleic acid)

P38, Tri-n-propyltin ester of poly(methyl vinyl ether/ maleic acid)

P39, Tri-n-propyltin ester of poly (methyl vinyl ether/ maleic acid)

P40, Poly(triphenyl lead methacrylate/methyl methacrylate)

P41, Poly(tri-n-butyltin methacrylate)

P42, Poly(tri-n-butyltin methacrylate/methyl methacrylate)

P43, Poly(tri-n-butyltin methacrylate/methyl methacrylate)

P44, Poly(tri-n-butyltin methacrylate/1H, 1H, 7H-dodecafluoroheptyl acrylate)

P45, Poly(tri-n-butyltin methacrylate/methyl methacrylate)
P92, Poly(tributyltin butadiene)
M1, 1:1 (by weight) mixture of P29/P34
M2, 1:1:1 (by weight) mixture of P13/P17/P31
M3, 1:1 (by weight) mixture of P20/P25
M4, 1:1 (by weight) mixture of P36/P38
M5, 1:1 (by weight) mixture of P37/P39
M10, 1:1 (by weight) mixture of P4/P24
M11, 1:1:1:1 (by weight) mixture of P4/P16/P24/P28
P4, Poly(tri-n-butyltin acrylate/tri-n-propyltin acrylate)
P28, Poly(triphenyltin acrylate)
P29, Poly(tri-n-butyltin methacrylate).

The preparation of the following organometallic polymers is given in reference (b).

S4-S9,S11, Poly(tri-n-butyltin methacrylate/styrene)
S10, Poly(tri-n-butyltin methacrylate)
P51, P62, Poly(tri-n-butyltin methacrylate/tri-n-propyltin methacrylate/methyl methacrylate)
P52, P53, Polycondensation product of maleic anhydride, propylene glycol and ethylene glycol crosslinked by tri-n-butyltin methacrylate
P54, Polycondensation product of sebacic acid and butenediol crosslinked by tri-n-butyltin methacrylate
P56, Polycondensation product of maleic anhydride and D-sorbitol crosslinked by tri-n-butyltin methacrylate
P59, P61, Polycondensation product of maleic anhydride, azelaic acid and propylene glycol crosslinked by tri-n-butyltin methacrylate.

Since the preparation of the organometallic polyvinyls is similar, the preparation of P63, the tri-n-butyltin ester of poly(ethylene/acrylic acid), is given in detail as an example:
P63, Tri-n-butyltin ester of poly(ethylene/acrylic acid).

The reaction was carried out in a 1-liter, 3-necked flask, provided with an azeotropic distillation head connected to a reflux condenser, a thermometer positioned such that it read the temperature of the reaction solution, and a stopper. The reaction solution was stirred by means of a magnetic stirrer. In the reaction flask, poly(ethylene/acrylic acid)[1] (0.25 mole acid, based on percent acid in the polymer) was added to a solution of tri-n-butyltin oxide (0.125 mole) and cyclohexane

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[1] Union Carbide EAA-9300 (high molecular weight).

(500 ml). The reaction was refluxed for 24 hours. The resultant clear organometallic polymer was cast in a film from the cyclohexane solution. The analysis calculated for P63 was: 18.2% Sn.

P64, Tri-n-butyltin Ester of Poly (Ethylene/Acrylic Acid)

P64 was prepared similar to P63 except that a lower molecular weight poly(ethylene/acrylic acid)[1] was employed. Tri-n-butyltin oxide (0.05 mole) reacted with poly(ethylene/ acrylic acid) (0.1 mole acid) in cyclohexane (350 ml). The product polymer was again clear and was cast as a film from the cyclohexane solution. The analysis calculated for P64 was: 18.1% Sn.

P65, Tri-n-butyltin Ester of Poly(Methyl Vinyl Ether/Ethyl Maleate/Maleic Acid)

P65 was prepared by the general method described above. In this synthesis, tri-n-butyltin oxide (0.05 mole) reacted with the ethyl half ester of poly (methyl vinyl ether/maleic acid; GAF Gantrez ES 225) (0.1 mole acid) in cyclohexane (150 ml). The product polymer was clear and was cast as a film from the cyclohexane solution. The analysis calculated for P65 was: 24.3% Sn.

P68, Tri-n-butyltin Ester of Poly(Vinyl Acetate/Crotonic Acid)

P68 was prepared by the general method described above. In this synthesis, tri-n-butyltin oxide (0.0146 mole) reacted with poly(vinyl acetate/crotonic acid); (Monsanto Gelva C5V16) (0.0291 mole acid) in benzene (300 ml). The product polymer was clear and was cast as a film from the benzene solution. The analysis for P68 was: 6.0% Sn.

P69, Tri-n-butyltin Ester of Poly(Vinyl Chloride/Vinyl Acetate/ Maleic Acid)

P69 was prepared by the general method described above. In this synthesis, tri-n-butyltin oxide (0.023 mole) reacted with poly(vinyl chloride/vinyl acetate/maleic acid)[2] (0.023 mole acid) in dichloromethane (200 ml). The product polymer was clear and was cast as a film from the dichloromethane solution. The analysis calculated for P69 was: 8.6% Sn.

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[1] Union Carbide EAA-9500 (low molecular weight).
[2] Union Carbide VMCA QEX-2032 (5.3% acid by weight).

P71, Tri-n-butyltin Ester of Poly(Vinyl Chloride/Vinyl Acetate/
    Maleic Acid)

P71 was prepared by the general method described above. In
this synthesis, tri-n-butyltin oxide (0.0086 mole) reacted with
poly(vinyl chloride/vinyl acetate/maleic acid)[1] (0.0086 mole
acid) in dichloromethane (200 ml). The product polymer was
clear and was cast as a film from the dichlomethane solution.
The analysis calculated for P71 was: 3.7% Sn.

P106, Tri-n-butyltin Ester of Poly(Methyl Vinyl Ether/Maleic
    Anhydride)

P106 was prepared by the general method described above.
In this synthesis, tri-n-butyltin oxide (0.05 mole) reacted with
poly(methyl vinyl ether/maleic anhydride; Polysciences) (0.05
mole) in cyclohexane. The product polymer was clear and was
cast as a film from the cyclohexane solution. The analysis
calculated for P106 was: 31.7% Sn.

Since the preparation of organometallic polyacrylates and
polymethacrylates is similar, the preparation of P85, poly
(tri-n-butyltin methacrylate/2-hydroxyethyl methacrylate), is
given in detail as an example.

P85, Poly(Tri-n-butyltin Methacrylate/2-Hydroxyethyl
    Methacrylate)

Tri-n-butyltin methacrylate (melting point 18° C) was
synthesized according to Montermoso, reference (c). The
polymerization reaction was carried out in a 1-liter, 3-necked
flask equipped with a reflux condenser, a thermometer (such
that it read the temperature of the reactants), and a stopper.
The reaction mixture was stirred by means of a magnetic stirrer.
Tri-n-butyltin methacrylate (0.1 mole), 2-hydroxyethyl
methacrylate (0.1 mole), and dibenzoyl peroxide (0.5% by weight)
were reacted in benzene (350 ml). The solution polymerization
was allowed to reflux for 24 hours. The resultant transparent
organometallic polymer was cast in a film from the benzene
solution. The analysis calculated for P85 was: 23.6% Sn.

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[1]Union Carbide VMCA (2.0% acid by weight).

P86, Poly(Tri-n-butyltin Methacrylate/2-Hydroxyethyl Acrylate)

P86 was prepared similar to P85. In this synthesis, tri-n-butyltin methacrylate (0.075 mole), 2-hydroxyethyl acrylate (0.075 mole), and dibenzoyl peroxide (0.5%) were reacted in benzene (350 ml). The solution polymerization was allowed to reflux for 24 hours. The resultant transparent organometallic polymer was cast in a film from the benzene solution. The analysis calculated for P85 was: 24.1% Sn.

P87, Poly(Tri-n-butyltin Methacrylate/2-Hydroxypropyl
    Methacrylate)

P87 was prepared by the general method described above. In this synthesis, tri-n-butyltin methacrylate (0.075 mole), 2-hydroxypropyl acrylate (0.075 mole), and dibenzoyl peroxide (0.5%) were reacted in benzene (350 ml). The solution polymerization was allowed to reflux for 24 hours. The resultant transparent organometallic polymer was cast in a film from the benzene solution. The analysis calculated for P87 was: 23.5% Sn.

P89, Poly(Tri-n-butyltin Methacrylate/2-Hydroxypropyl
    Methacrylate)

P89 was prepared by the general method described above. In this synthesis, tri-n-butyltin methacrylate (0.075 mole), 2-hydroxypropyl methacrylate (0.075 mole), and dibenzoyl peroxide (0.5%) were reacted in benzene (350 ml). The solution polymerization was allowed to reflux for 24 hours. The resultant transparent organometallic polymer was cast in a film from the benzene solution. The analysis calculated for P89 was: 22.8% Sn.

P90, Poly(Tri-n-butyltin Methacrylate/1,4-Butanediol
    Monoacrylate)

P90 was prepared by the general method described above. In this synthesis, tri-n-butyltin methacrylate (0.075 mole), 1,4-butanediol monoacrylate (0.075 mole), and dibenzoyl peroxide (0.5%) were reacted in benzene (350 ml). The solution polymerization was allowed to reflux for 24 hours. The resultant transparent organometallic polymer was cast in a film from the benzene solution. The analysis calculated for P90 was: 22.2% Sn.

P91, Poly(Tri-n-butyltin Methacrylate/Methyl Methacrylate)

P91 was prepared by the general method described above. In this synthesis, tri-n-butyltin methacrylate (0.1 mole), methyl methacrylate (0.05 mole), and dibenzoyl peroxide (0.5%) were reacted in cyclohexane (125 ml) for 24 hours. The resultant transparent organometallic polymer was cast in a film from the cyclohexane solution. The analysis calculated for P91 was: 27.9% Sn.

P92, Poly(Tri-n-propyltin Methacrylate/Methyl Methacrylate)

Tri-n-propyltin methacrylate was synthesized according to Montermoso, reference (c). P92 was prepared by the general method described above. In this synthesis, tri-n-propyltin methacrylate (0.1 mole), methyl methacrylate (0.05 mole), and dibenzoyl peroxide (0.5%) were reacted in cyclohexane (100 ml) for 24 hours. The resultant transparent organometallic polymer was cast in a film from the cyclohexane solution. The analysis calculated for P92 was: 31.0% Sn.

P93, Poly(Tri-n-butyltin Methacrylate/Tri-n-propyltin Methacrylate/Methyl Methacrylate)

P93 was prepared by the general method described above. In this synthesis, tri-n-butyltin methacrylate (0.05 mole), tri-n-propyltin methacrylate (0.05 mole), methyl methacrylate (0.05 mole), and dibenzoyl peroxide (0.5%) were reacted in cyclohexane (125 ml) for 24 hours. The resultant transparent organometallic polymer was cast in a film from the cyclohexane solution. The analysis calculated for P93 was: 29.3% Sn.

P94, Poly(Triphenyltin Methacrylate/Tri-n-butyltin Methacrylate/Methyl Methacrylate)

Triphenyltin methacrylate was synthesized according to Dyckman, et al, reference (a). P94 was prepared by the general method described above. In this synthesis, triphenyltin methacrylate (0.025 mole), tri-n-butyltin methacrylate (0.025 mole), methyl methacrylate (0.025 mole), and dibenzoyl peroxide (0.5%) were reacted in benzene (100 ml) for 24 hours. The resultant transparent organometallic polymer was cast in a film from the benzene solution. The analysis calculated for P94 was: 26.2% Sn.

P95, Poly(Triphenyltin Methacrylate/Methyl Methacrylate)

P95 was prepared by the general method described above. In this synthesis, triphenyltin methacrylate (0.0364 mole), methyl methacrylate (0.0182 mole), and dibenzoyl peroxide (0.5%) were reacted in benzene (100 ml) for 24 hours. The resultant transparent organometallic polymer was cast in a film from the benzene solution. The analysis calculated for P95 was: 24.5% Sn.

P96, Poly(Triphenyltin Methacrylate/Tri-n-propyltin Methacrylate/ Methyl Methacrylate)

P96 was prepared by the general method described above. In this synthesis, triphenyltin methacrylate (0.027 mole), tri-n-propyltin methacrylate (0.027 mole), methyl methacrylate (0.027 mole), and dibenzoyl peroxide (0.5%) were reacted in benzene (300 ml) for 24 hours. The resultant transparent organometallic polymer was cast in a film from the benzene solution. The analysis calculated for P96 was: 27.2% Sn.

P97, Poly(Triphenyltin Methacrylate/Tri-n-butyltin Methacrylate/ Tri-n-propyltin Methacrylate/Methyl Methacrylate)

P97 was prepared by the general method described above. In this synthesis, triphenyltin methacrylate (0.02 mole), tri-n-butyltin methacrylate (0.02 mole), methyl methacrylate (0.03 mole), and dibenzoyl peroxide (0.5%) were reacted in benzene (300 ml) for 24 hours. The resultant transparent organometallic polymer was cast in a film from the benzene solution. The analysis calculated for P97 was: 27.6% Sn.

P99, Poly(Triphenyllead Methacrylate/Methyl Methacrylate)

Triphenyllead methacrylate (melting point 129° C) was synthesized according to the preparation given by Dyckman, et al, reference (a). Triphenyllead hydroxide (0.2 mole) and methacrylic acid (0.2 mole) were reacted in benzene (700 ml). P99 was prepared by the general method described above. In this synthesis, triphenyllead methacrylate (0.06 mole), methyl methacrylate (0.06 mole), and dibenzoyl peroxide (0.5%) were reacted in benzene (150 ml) for 24 hours. The resultant transparent organometallic polymer was cast in a film from the benzene solution. The analysis calculated for P99 was: 33.3% Pb.

P100, Poly(Tri-n-butyltin Methacrylate/Triphenyllead
Methacrylate/Methyl Methacrylate)

P100 was prepared by the general method described above.
In this synthesis, tri-n-butyltin methacrylate (0.1 mole),
triphenyllead methacrylate (0.1 mole), methyl methacrylate
(0.1 mole), and dibenzoyl peroxide (0.5%) were reacted in
benzene (350 ml) for 24 hours. The resultant transparent
organometallic polymer was cast in a film from the benzene
solution. The analysis calculated for P100 was: 11.9% Sn;
20.7% Pb.

P103, Poly(Tri-n-butyltin Methacrylate/Vinyl Acetate)

P103 was prepared by the general method described above.
In this synthesis, tri-n-butyltin methacrylate (0.1 mole), vinyl
acetate (0.1 mole), and dibenzoyl peroxide (0.5%) were reacted
in cyclohexane (200 ml) for 24 hours. The resultant transparent
organometallic polymer was cast in a film from the benzene
solution. The analysis calculated for P103 was: 25.7% Sn.

P104, Poly(Pentachlorophenol Acrylate/Methyl Methacrylate)

Pentachlorophenol acrylate (melting point 54° C) was
synthesized as follows. The sodium salt of pentachlorophenol
(0.1 mole) and acryloyl chloride (0.1 mole) were reacted in
benzene (400 ml). Following isolation of the product, penta-
chlorophenol acrylate (0.1 mole), it was reacted with methyl
methacrylate (0.1 mole) and dibenzoyl peroxide (1.0%) in
benzene (300 ml) for 24 hours. The resultant transparent
polymer was cast in a film from benzene solution. The analysis
calculated for P104 was: 40.8% Cl.

P105, Poly(Tri-n-butyltin Methacrylate/Pentachlorophenol
Acrylate/Methyl Methacrylate)

P105 was prepared by the general method described above.
In this synthesis, tri-n-butyltin methacrylate (0.1 mole),
pentachlorophenol acrylate (0.1 mole), methyl methacrylate
(0.1 mole), and dibenzoyl peroxide (1.0%) were reacted in
cyclohexane (300 ml) for 24 hours. The resultant transparent
organometallic polymer was cast in a film from the benzene
solution. The analysis calculated for P105 was: 14.7% Sn;
21.9% Cl.

P62, Poly(Tribenzyltin Methacrylate/Tri-n-butyltin Methacrylate/
   Tri-n-propyltin Methacrylate/Methyl Methacrylate)

An equimolar mixture of tribenzyltin methacrylate, tri-n-
propyltin methacrylate, and tri-n-butyltin methacrylate was
prepared by reaction of tribenzyltin hydroxide (0.05 mole), tri-
n-butyltin oxide (0.025 mole), tri-n-propyltin oxide (0.025
mole), and methacrylic acid (0.15 mole) in benzene (200 ml).
The water of reaction was removed by azeotropic distillation
under vacuum, as in reference (c). P62 was prepared by the
general method described above. In this synthesis, methyl
methacrylate (0.075 mole) and dibenzoyl peroxide (0.5%) were
added to the equimolar mixture of three organometallic monomers.
The benzene solution was heated for 24 hours. The resultant
translucent organometallic polymer was cast in a film from the
benzene solution. The analysis calculated for P62 was: 26.6% Sn.

Crosslinked unsaturated polyesters were also prepared.
The synthesis for the following organometallic polymer is given
in detail in reference (b).

P70, Polycondensation Product of Sebacic Acid and Butenediol
   Crosslinked by Tri-n-butyltin Methacrylate

P70 was prepared as in reference (b). In this synthesis,
equimolar quantities of sebacic acid (0.3 mole) and 2-butene-
1,4-diol (0.3 mole) underwent polycondensation. Dibenzoyl
peroxide (0.5% total weight of reactants) was dissolved in tri-
n-butyltin methacrylate (0.3 mole). While the unsaturated alkyd
was warm (between 70° and 80° C), it and the tri-n-butyltin
methacrylate were degassed by placing them in a vacuum.
Following the degassing procedure, the unsaturated alkyd and the
tri-n-butyltin methacrylate were mixed and poured into a metal
mold. The mold, composed of two steel plates with a 6- x 6- x
3/16-inch cavity between them, was treated with Dow Corning
release agent XR43130. The filled mold, fastened with steel
bolts, was heated to 40° C for 14 hours, followed by 80° C for
6 hours, as in reference (d). The resultant polymer was a
white solid. The analysis calculated for P70 was: 18.8% Sn.

Since the preparation of the following organometallic
polyesters is similar, the preparation of P80, unsaturated
polyester resin Hetron 22992 crosslinked by styrene, and tri-n-
butyltin methacrylate is given in detail.

P80, Unsaturated Polyester Resin Hetron 22992 Crosslinked by Tri-n-butyltin Methacrylate

Unsaturated polyester resin Hetron 22992 contains 28% by weight styrene to which up to 15 pph of a vinyl monomer may be added for crosslinking. In this reaction, Hetron 22992 (85 grams) reacted with tri-n-butyltin methacrylate (15 grams). The polymerization was catalyzed by MEKP (1 pph) and was promoted by Cobalt napthenate Lupersol DDM (0.2 pph) at room temperature. The reaction mixture was poured onto a 10- x 12-inch panel having a 1/16-inch-deep border of asphalt tape around its outer edges. The reaction mixture gelled on the panel surface within 1 hour and was left undisturbed for 24 hours, reference (e). The resultant transparent organometallic polymer was a dry, hard film. The analysis calculated for P80 was: 4.8% Sn.

P81, Unsaturated Polyester Resin Hetron 22992 Crosslinked by Tri-n-butyltin Methacrylate

P81 was prepared by the general method described above. In this synthesis, Hetron 22992 (85 grams) reacted with tri-n-butyltin methacrylate (30 grams), MEKP (1.0 pph), and cobalt napthenate Lupersol DDM (0.2 pph). The resultant transparent organometallic polymer was a wet-surfaced, hard film. The analysis calculated for P81 was: 8.3% Sn.

P82, Unsaturated Polyester Resin Hetron 22992 Crosslinked by Tri-n-butyltin Methacrylate and Styrene

P82 was prepared by the general method described above. In this synthesis, Hetron 22992 (85 grams) reacted with tri-n-butyltin methacrylate (8 grams), styrene (7 grams), MEKP (1.0 pph), and cobalt napthenate Lupersol DDM (0.2 pph). The resultant transparent organometallic polymer was a dry, hard film. The analysis calculated for P82 was: 2.5% Sn.

P83, Unsaturated Polyester Resin Hetron 31 Crosslinked by Tri-n-butyltin Methacrylate

P83 was prepared by the general method described above. In this synthesis, Hetron 31 (85 grams) reacted with tri-n-butyltin methacrylate (15 grams), MEKP (1.0 pph), and cobalt napthenate Lupersol DDM (0.2 pph). The resultant transparent organometallic polymer was a dry, hard film. The analysis calculated for P83 was: 4.8% Sn.

P84, Unsaturated Polyester Resin Hetron 31 Crosslinked by Tri-
n-butyltin Methacrylate

P84 was prepared by the general method described above.
In this synthesis, Hetron 31 (92 grams) reacted with tri-n-
butyltin methacrylate (8 grams), MEKP (1.0 pph), and cobalt
napthenate Lupersol DDM (0.2 pph). The resultant transparent
organometallic polymer was a dry, hard film. The analysis
calculated for P84 was: 2.5% Sn.

Each of the following organometallic epoxy resins has
unique preparations.

P88, Epoxy Resin Based on Cycloaliphatic Epoxide ERL-4221
Crosslinked by Poly(Tri-n-butyltin Methacrylate/
Methacrylic Acid)

Poly(tri-n-butyltin methacrylate/methacrylic acid) was
prepared similar to P85. In this synthesis, tri-n-butyltin
methacrylate (0.15 mole), methacrylic acid (0.15 mole), and
dibenzoyl peroxide (0.5%) were reacted in cyclohexane (500 ml).
The solution polymerization was allowed to reflux for 24 hours.
The resultant organometallic polymer was filtered, dried to a
white powder, and pulverized. In the preparation of P88,
ERL-4221 (reference (f)) (120 grams) and poly(tri-n-butyltin
methacrylate methacrylic acid) (120 grams) were mixed at room
temperature. The mixture was spread on a 10- x 12-inch panel
and cured in an oven at 100° C for 5 hours. The resultant
organometallic epoxy was a transparent, porous, hard film.
The analysis calculated for P88 was: 12.8% Sn.

P108 Epoxy Resin Based on Poly(Glycidyl Methacrylate/Tri-n-
butyltin Methacrylate) Cured by 1,8-Methanediamine

Poly(glycidyl methacrylate/tri-n-butyltin methacrylate)
was prepared similar to P85. In this synthesis, glycidyl
methacrylate (0.07 mole), tri-n-butyltin methacrylate (0.07
mole), and 2,2-azo-bisisobutyronitrile (0.6%) were reacted in
toluene (90 ml) at 75° C for 16 hours. The epoxy equivalent
for poly(glycidyl methacrylate/tri-n-butyltin methacrylate)
is 1900, and the equivalent weight of 1,8-methanediamine is
42.5. After the toluene solution of poly(glycidyl methacrylate/
tri-n-butyltin methacrylate) was cooled to room temperature,
0.69 gram (2.25 pph) of 1,8-methanediamine was added, and this
solution was allowed to mix overnight and was then heated at
96° C for 3 hours. The resultant clear organometallic polymer
was cast in a film from the toluene solution. The analysis
calculated for P108 was: 22.4% Sn.

P109, Epoxy Resin Based on Poly(Allyl Glycidyl Ether/Tri-n-butyltin Methacrylate) and Epon 828 Crosslinked by Triethylenetetramine

Poly(allyl glycidyl ether/tri-n-butyltin methacrylate) was prepared similar to P85. In this synthesis, allyl glycidyl ether (0.07 mole), tri-n-butyltin methacrylate (0.07 mole), and 2,2-azo-bisisobutyronitrile (0.6%) were reacted in toluene (90 ml) at 75° C for 16 hours. The toluene was then allowed to evaporate at room temperature from the polymer. The epoxy equivalent for Epon 828 (Shell Chemicals) is 189, and the equivalent weight of triethylenetetramine is 24.2. To a mixture of poly(allyl glycidyl ether/tri-n-butyltin methacrylate) (22.5 grams) and Epon 828 (21.6 grams), 4.04 grams (12.8 pph) of TETA were added and mixed well. The resultant viscous mixture was spread on a 10- x 12-inch panel, let stand at room temperature overnight, and was then heated at 80° C for 3 hours. The resultant clear organometallic polymer was a hard, yellow film. The analysis calculated for P109 was: 12.7% Sn.

P110, Epoxy Resin Based on Poly(Allyl Glycidyl Ether/Tri-n-butyltin Methacrylate/Methyl Methacrylate) and Epon 828 Crosslinked by Triethylenetetramine

Poly(allyl glycidyl ether/tri-n-butyltin methacrylate/methyl methacrylate) was prepared similar to P85. In this synthesis, allyl glycidyl ether (0.035 mole), tri-n-butyltin methacrylate (0.07 mole), methyl methacrylate (0.07 mole), and 2,2-azobisisobutyronitrile (0.6%) were reacted in toluene (90 ml) at 75° C for 16 hours. The toluene was allowed to evaporate at room temperature from the polymer. To a mixture of poly(allyl glycidyl ether/tri-n-butyltin methacrylate/methyl methacrylate) (38.5 grams) and Epon 828 (71.5 grams), 9.15 grams (12.8 pph) of TETA were added and mixed well. The resultant viscous mixture was spread on a 10- x 12-inch panel, let stand overnight, and was then heated at 80° C for 3 hours. The resultant clear organometallic polymer was a hard, yellow film. The analysis calculated for P110 was: 9.9% Sn.

P111, Epoxy Resin Based on 80% Tri-n-butyltin Ester of Poly(Methyl Vinyl Ether/Maleic Acid) and Epon 828 Crosslinked by Triethylenetetramine

The 80% tri-n-butyltin ester of poly(methyl vinyl ether/maleic acid) was prepared similar to P63. In this synthesis, tri-n-butyltin oxide (0.16 mole) reacted with poly(methyl vinyl ether/maleic acid; GAF S95) (0.2 mole acid) in cyclohexane

(500 ml). The cyclohexane was allowed to evaporate at room
temperature from the polymer. To a mixture of the 80% tri-n-
butyltin ester of poly(methyl vinyl ether/maleic acid)
(35.5 grams) and Epon 828 (34.7 grams), 4.44 grams (12.8 pph)
of TETA were added and mixed well. The resultant viscous
mixture was spread on half of a 10- x 12-inch panel, let
stand overnight, and was then heated at 70° C for 6 hours and
at 50° C for 10 hours. The resultant organometallic polymer was
a hard, nonhomogenous film. The analysis calculated for P111
was: 14.6% Sn.

P112, Epoxy Resin Based on 80% Tri-n-butyltin Ester of Poly
      (Methyl Vinyl Ether/Maleic Acid) and DEN 438 Crosslinked
      by Triethylenetetramine

The same 80% tri-n-butyltin ester of poly(methyl vinyl
ethyl/maleic acid) prepared for P111 was used here. This
polymer was precipitated from cyclohexane solution using
methanol and allowed to dry. To a mixture of the 80% tri-n-
butyltin ester of poly(methyl vinyl ether/maleic acid)
(82.70 grams) and DEN 438 (Union Carbide) (87.65 grams),
22.7 grams (28 pph) of curing agent DEH 50 (Union Carbide)
were added; the mixture was heated and, at 74° C, the DEH 50
melted into the mixture. The resultant viscous mixture was
spread on a 10- x 12-inch panel, let stand overnight, and was
then heated at 70° C for 6 hours and 50° C for 16 hours. The
resultant organometallic polymer was a hard, yellow, opaque,
homogenous film. The analysis calculated for P112 was:
13.1% Sn.

The following organometallic epoxy resins were prepared
under contract for the Center by the State University of
Washington. Since their synthesis is described in reference
(g), only a brief summary of the synthesis and a list of the
polymers will be given. The synthesis involved the partial
esterification of carboxyl-containing polymers with tri-n-
butyltin oxide in a first step. The resultant organotin
polymers were then employed as curing agents for epoxy monomers
in a second step. In some preparations, where the epoxy monomer
contained a double bond (e.g., glycidyl methacrylate), styrene
was added to help form a crosslinked network structure. In
preparations where anhydride groups, in the organotin polymer,
themselves did not react with epoxy groups (e.g., Epon 828),
accelerators containing hydroxyl groups (e.g., tri(dimethyl-
aminomethyl) phenol (DMP-30), ethylene glycol) were used to open
the anhydride to form acid groups, which could initiate

polymerization of the epoxy groups. Different ratios of free carboxyl to epoxide groups were used and, in some preparations, additional catalysis was provided (e.g., benzyl dimethyl amine). In each preparation, viscous mixtures of reactants were poured on 10- x 12-inch panels and heated near 100° C for varying periods of time.

WS41, 60% Tri-n-butyltin Ester of Poly(Methyl Vinyl Ether/ Maleic Acid), Styrene,and Glycidyl Methacrylate

WS42, 40% Tri-n-butyltin Ester of Poly(Methyl Vinyl Ether/ Maleic Acid), Styrene,and Glycidyl Methacrylate

WS51, 80% Tri-n-butyltin Ester of Poly(Methyl Vinyl Ether/ Maleic Acid), Styrene,and Glycidyl Methacrylate

WS52, 60% Tri-n-butyltin Ester of Poly(Methyl Vinyl Ether/ Maleic Acid), Styrene,and Glycidyl Methacrylate

WS61, 40% Tri-n-butyltin Ester of Poly(Methyl Vinyl Ether/ Maleic Acid), Styrene,and Glycidyl Methacrylate

WS62, 40% Tri-n-butyltin Ester of Poly(Methyl Vinyl Ether/ Maleic Anhydride), Styrene, Glycidyl Methacrylate, and Ethylene Glycol

WS63, 60% Tri-n-butyltin Ester of Poly(Methyl Vinyl Ether/ Maleic Anhydride), Styrene, Glycidyl Methacrylate, and DMP-30

WS71, 40% Tri-n-butyltin Ester of Poly(Methyl Vinyl Ether/ Maleic Anhydride), Styrene, Glycidyl Methacrylate, and Ethylene Glycol

WS81, 60% Tri-n-butyltin Ester of Poly(Hexene-1-Co-Maleic Anhydride), Styrene,and Glycidyl Methacrylate

WS82, 60% Tri-n-butyltin Ester of Poly(Styrene-Co-Maleic Anhydride), Styrene,and Glycidyl Methacrylate

WS91, 60% Tri-n-butyltin Ester of Poly(Hexene-1-Co-Maleic Anhydride), Styrene,and Glycidyl Methacrylate

WS101, 40% Tri-n-butyltin Ester of Poly(Styrene-Co-Maleic Anhydride), Styrene,and Glycidyl Methacrylate

WS102, 60% Tri-n-butyltin Ester of Poly(Styrene-Co-Maleic Anhydride), Styrene, Glycidyl Methacrylate, and Ethylene Glycol

WS111, 40% Tri-n-butyltin Ester of Poly(Hexene-1-Co-Maleic Anhydride), Styrene, Glycidyl Methacrylate, and Ethylene Glycol

WS112, 40% Tri-n-butyltin Ester of Poly(Styrene-Co-Maleic Anhydride), Styrene, Glycidyl Methacrylate, and Ethylene Glycol

WS121, 60% Tri-n-butyltin Ester of (Styrene-Co-Maleic Anhydride), Epon 828, and DMP-10

WS131, 40% Tri-n-butyltin Ester of Poly(Styrene-Co-Maleic Anhydride), Epon 828, ERL 4221, and DMP-10

WS141, 40% Tri-n-butyltin Ester of Poly(Styrene-Co-Maleic Anhydride), ERL 4221, and BDMA

WS142, 60% Tri-n-butyltin Ester of Poly(Styrene-Co-Maleic Anhydride), Epon 828, ERL 4221, and DMP10

WS151, 60% Tri-n-butyltin Ester of Poly(Styrene-Co-Maleic Anhydride), ERL 4221, and BDMA

WS152, 40% Tri-n-butyltin Ester of Poly(styrene-Co-Maleic Anhydride) ERL 4289, Epon 828, and BDMA

WS161, 60% Tri-n-butyltin Ester of Poly(Styrene-Co-Maleic Anhydride), ERL 4221, Epirez 5022 (Cellenese Plastics), and BDMA

WS162, 40% Tri-n-butyltin Ester of Poly(Styrene-Co-Maleic Anhydride), ERL 4221, Empirez 5022, and BDMA

WS163, 60% Tri-n-butyltin Ester of Poly(Styrene-Co-Maleic Anhydride) ERL 4289, Empirez 5022, and BDMA

The following describes the preparation of organometallic polyurethanes.

P120, Polyurethane Resin Based on Poly(Tri-n-butyltin Methacrylate/2-Hydroxypropyl Methacrylate), Toluene Di-isocyanate, and PRC Part A and Part B

Poly(tri-n-butyltin methacrylate/2-hydroxypropyl methacrylate) was prepared similar to P89. In this synthesis,

tri-n-butyltin methacrylate (0.193 mole), 2-hydroxypropyl methacrylate (0.193 mole), and dibenzoyl peroxide (0.5%) were reacted in benzene (700 ml). Five grams of the dried product was mixed with 20 grams of PRC part A.[1] Toluene di-isocyanate was mixed with 20 grams of PRC part B.[1] These two mixtures were combined and were coated on two 10- x 12-inch test panels. The analysis calculated for P120 was: 1.3% Sn.

P121, Polyurethane Resin Based on Poly(Tri-n-butyltin Methacrylate/2-Hydroxypropyl Methacrylate), TDI and PRC Part B

Poly(tri-n-butyltin methacrylate/2-hydroxypropyl methacrylate) was prepared as described in P120. Twenty-five grams of this polymer was mixed with 17 grams of PRC part B and 2.8 grams of TDI. This mixture was coated on two 10- x 12-inch test panels and was cured at room temperature. The analysis calculated for P121 was: 12.8% Sn.

P122, Polyurethane Resin Based on Poly(Tri-n-butyltin Methacrylate/2-Hydroxyethyl Acrylate), TDI, and Astrocoat 8006

Poly(tri-n-butyltin methacrylate/2-hydroxyethyl acrylate) was prepared similar to P86. In this synthesis, tri-n-butyltin methacrylate (0.1 mole), 2-hydroxyethyl acrylate (0.1 mole), and dibenzoyl peroxide (0.5%) were reacted in benzene (250 ml). The dried product was mixed with 174 grams of TDI at 30° C under a nitrogen atmosphere. Forty-three grams of this mixture was mixed with 553 grams of Astrocoat 8006,[2] spread on panels, and allowed to cure at room temperature. The analysis calculated for P122 was: 0.4% Sn.

P123, Polyurethane Resin Based on Poly(Tri-n-butyltin Methacrylate/2-Hydroxyethyl Acrylate), TDI, and Astrocoat 8006

In this synthesis, 218 grams of the same poly(tri-n-butyltin methacrylate/2-hydroxyethyl acrylate), TDI, and Astrocoat 8006 were mixed with 608 grams of astrocoat 8006. The reaction mixture was spread on 10- x 12-inch panels and allowed to cure at room temperature. The analysis calculated for P123 was: 1.4% Sn.

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[1] Products Research and Chemical Corp. Interim Tech Data Sheet PR-1654 (Parts A&B) (Apr 1973)
[2] J. Olin Chemical Corp. Tech Bulletin 8720 (Astrocast System 7600) (June 1973)

APPENDIX B
ANTIFOULING PERFORMANCE OF ORGANOMETALLIC POLYMERS
PEARL HARBOR, HAWAII, B1-B8
MIAMI BEACH, FLORIDA, B9-B10

4526

ORGANOMETALLIC POLYMER: __P13 (OMP 5)__
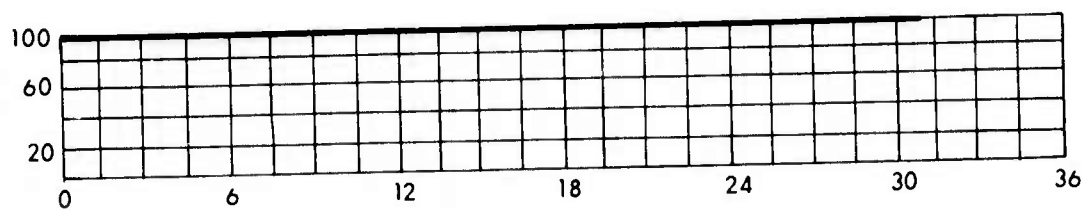
ORGANOMETALLIC POLYMER: __P20__
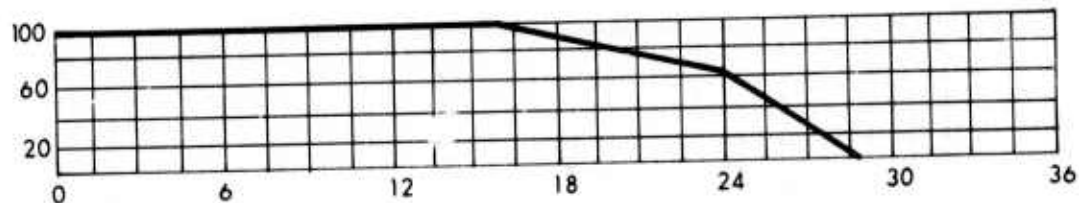
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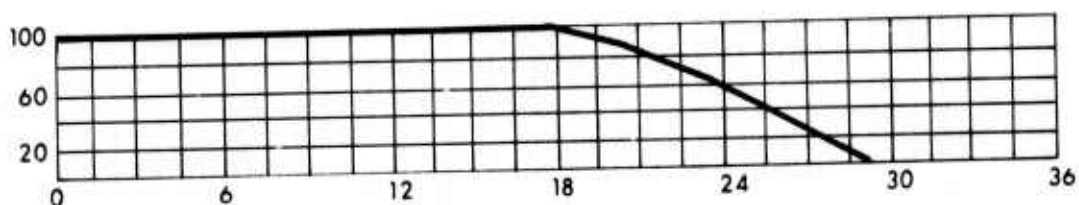
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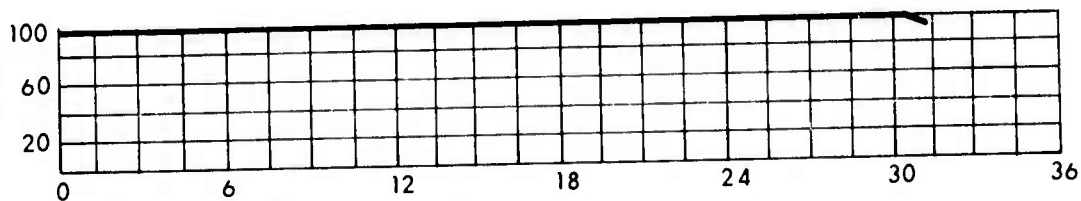
ORGANOMETALLIC POLYMER: __P36__

ANTIFOULING PERFORMANCE, %
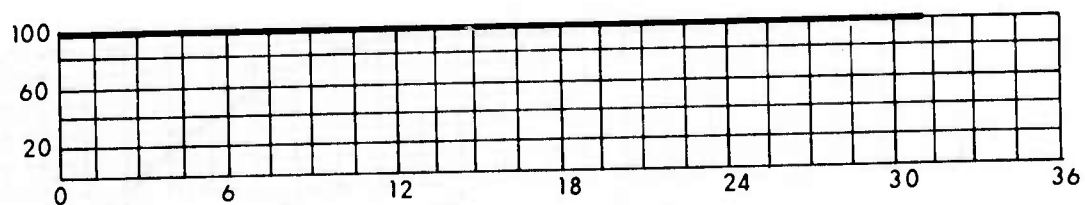
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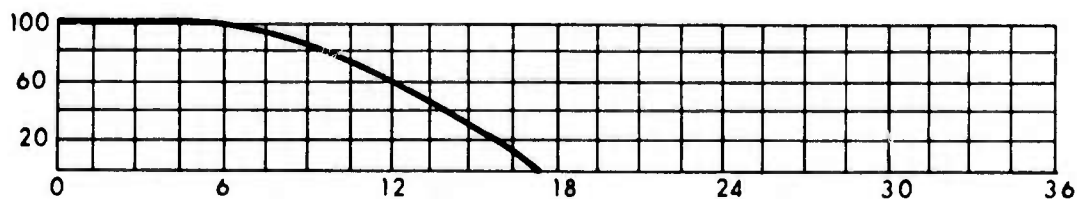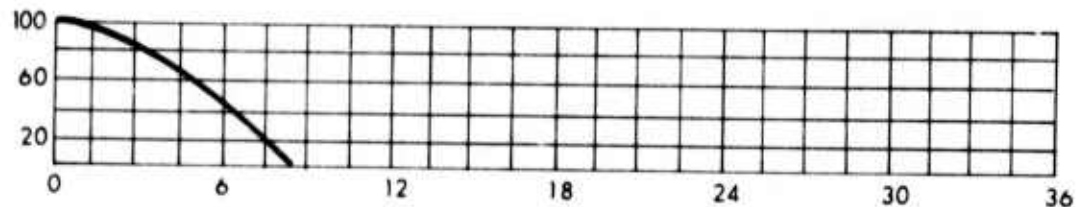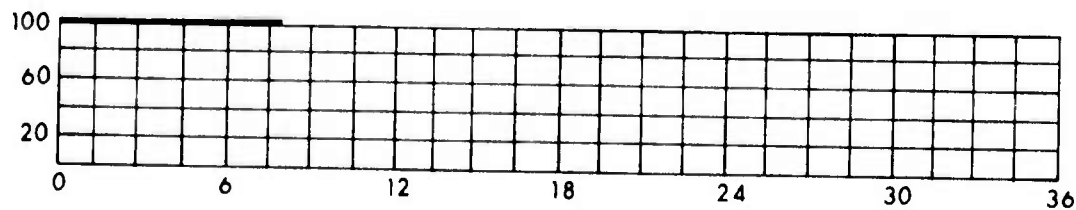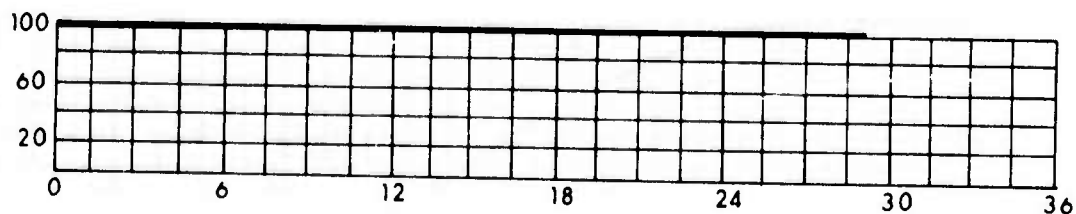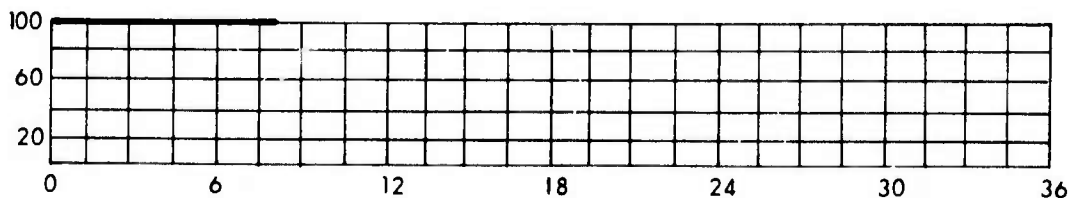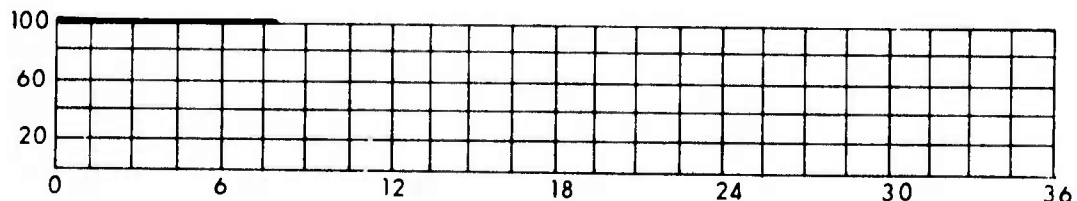ORGANOMETALLIC POLYMER: P37 (OMP 4)

ORGANOMETALLIC POLYMER: P38

ANTIFOULING PERFORMANCE, %
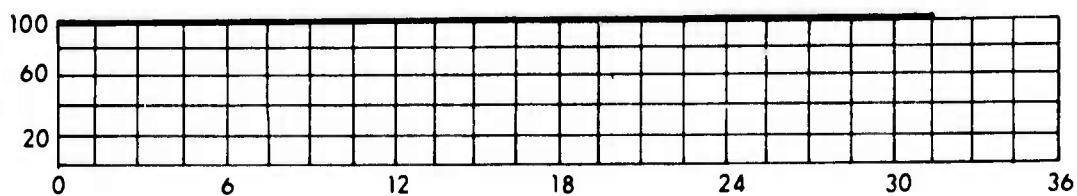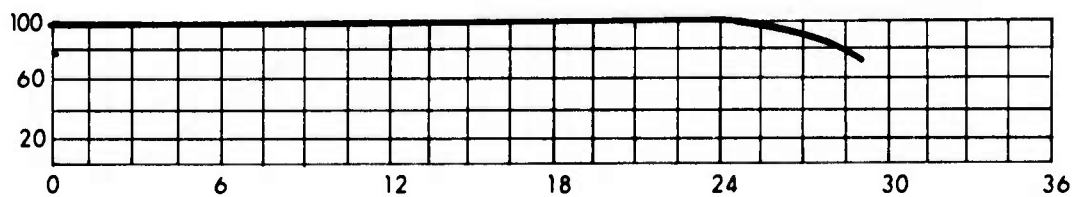
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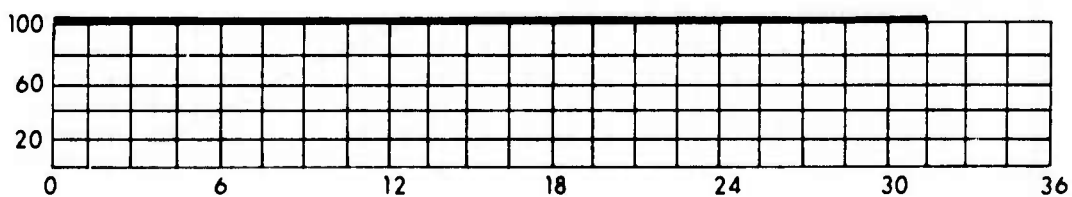
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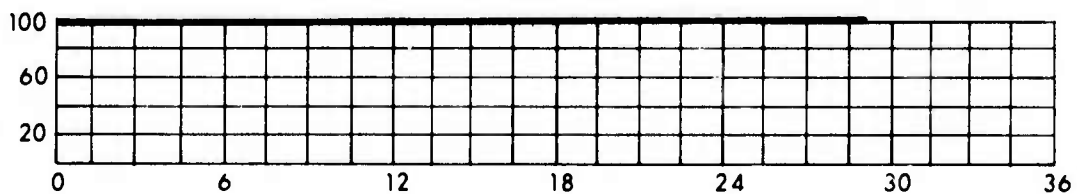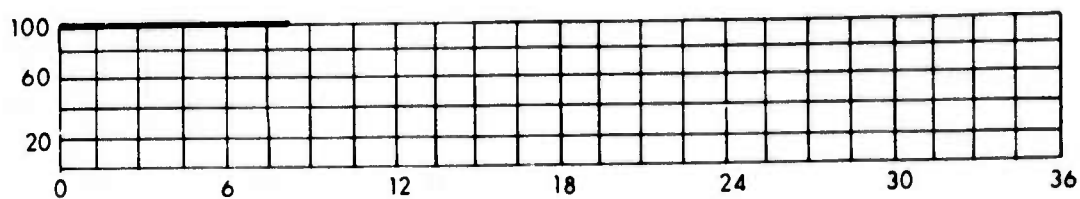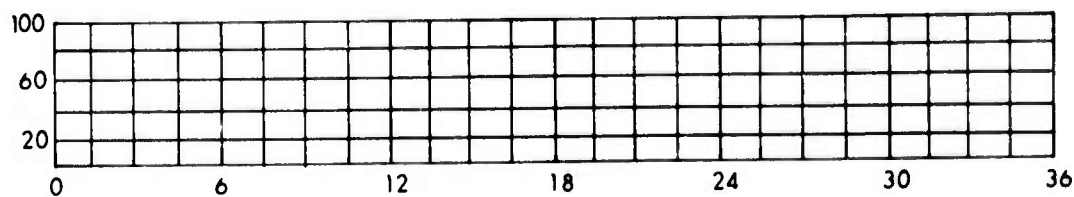
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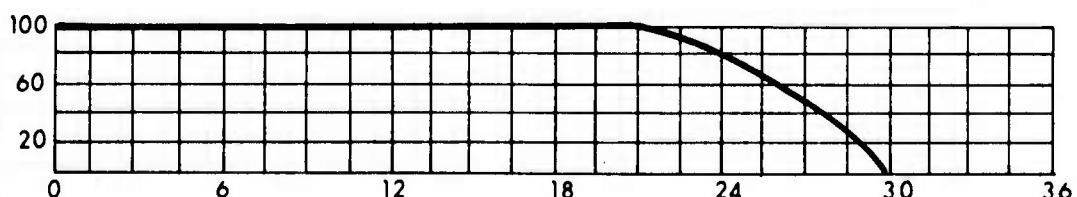
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ORGANOMETALLIC POLYMER: __P43 (OMP 2)__
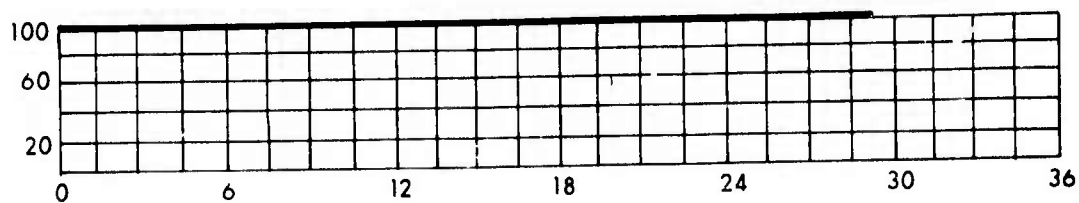
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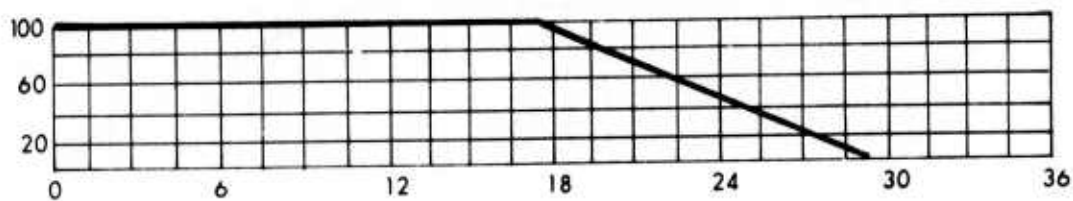
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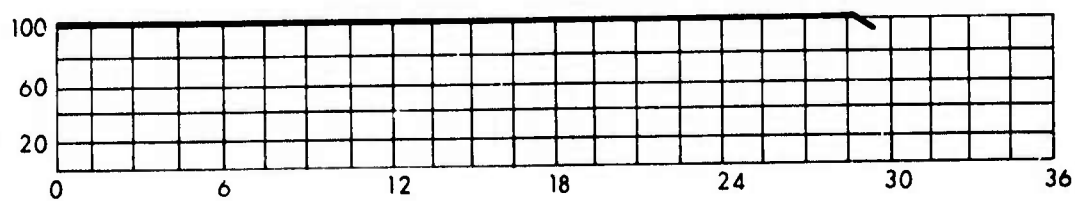
ORGANOMETALLIC POLYMER: __M1 (OMP 1)__
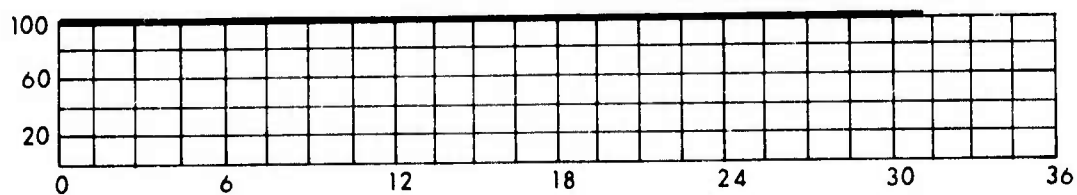
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ANTIFOULING PERFORMANCE, %
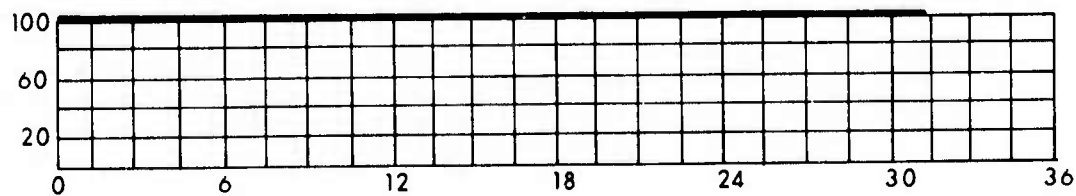
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ORGANOMETALLIC POLYMER: M5

ORGANOMETALLIC POLYMER: M10

ANTIFOULING PERFORMANCE, %
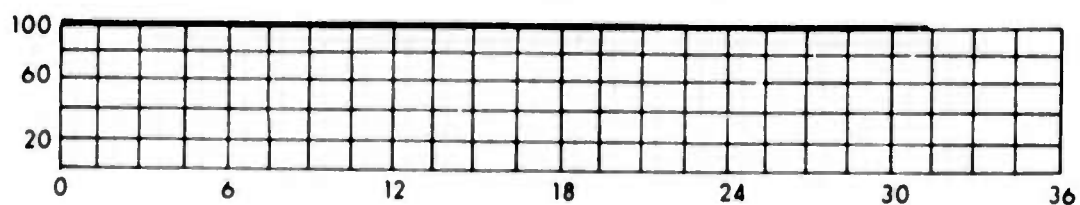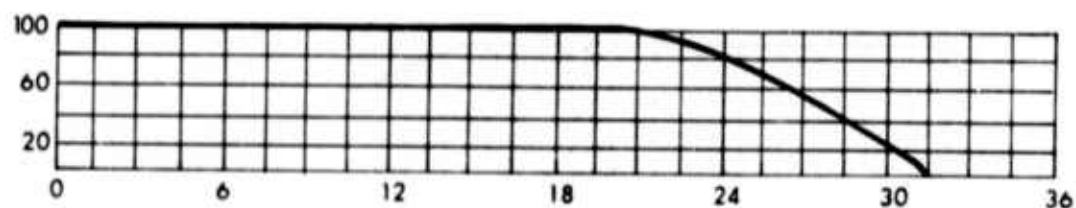
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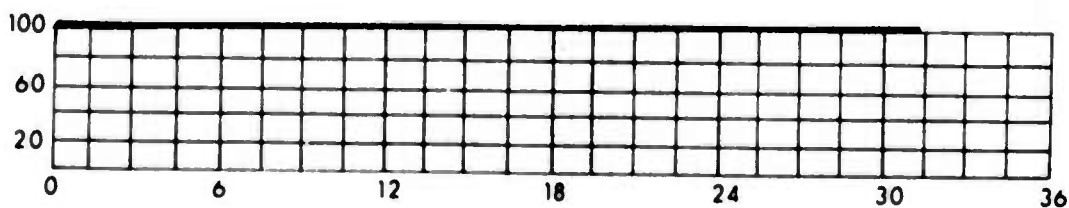
ORGANOMETALLIC POLYMER: S6
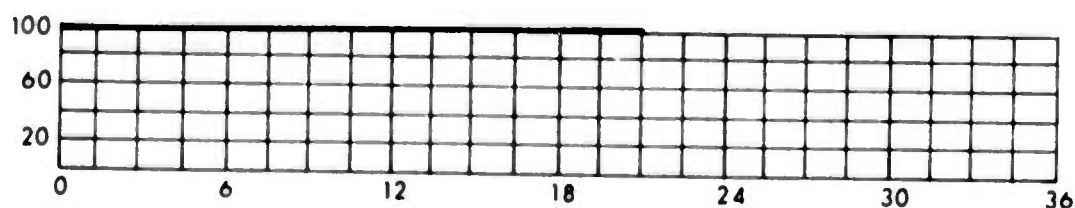
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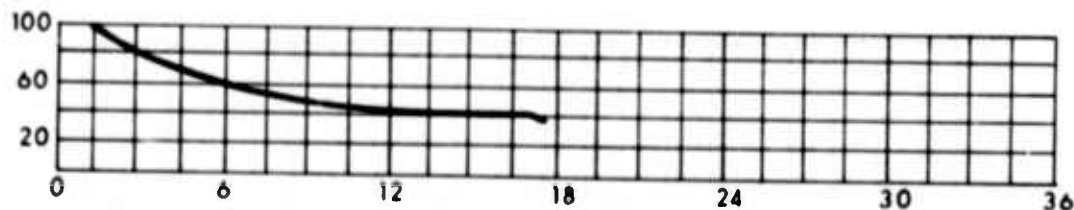
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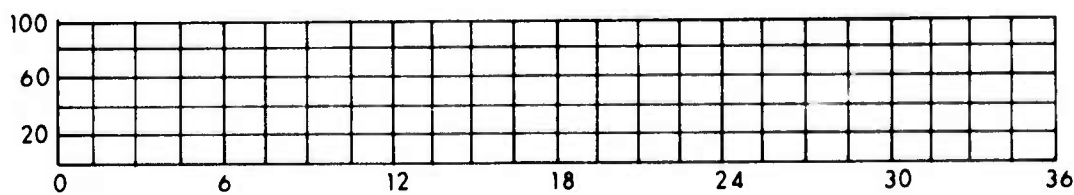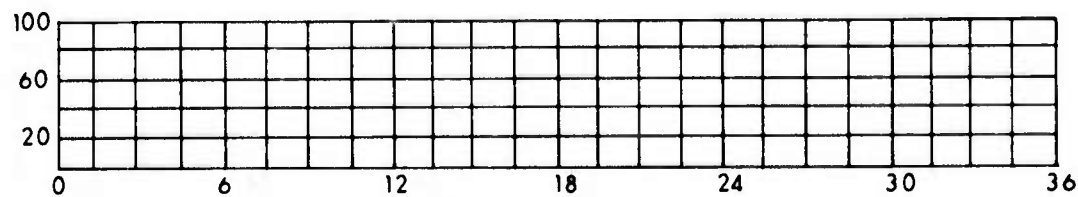
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ORGANOMETALLIC POLYMER: __S10__

ANTIFOULING PERFORMANCE, %
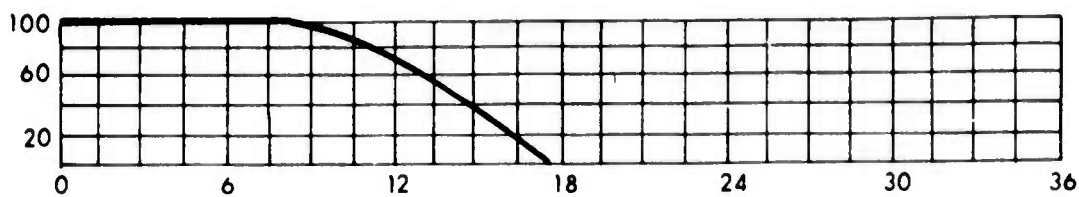
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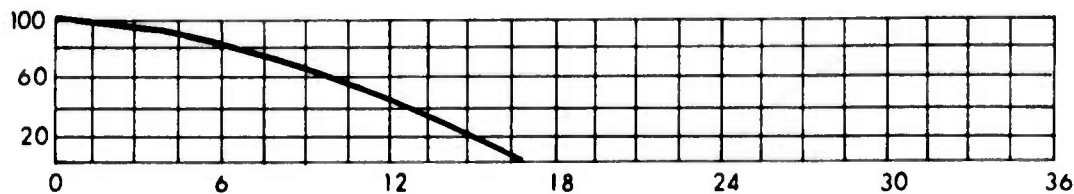
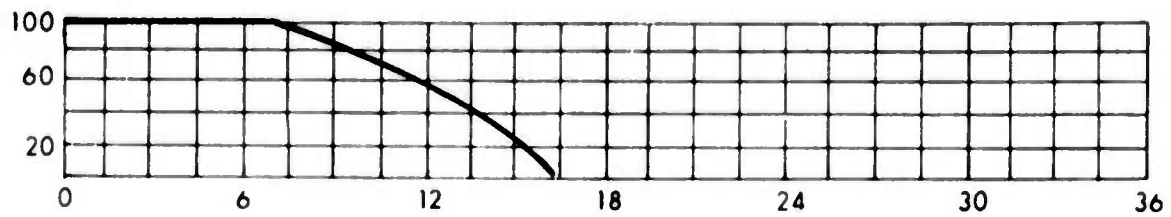ORGANOMETALLIC POLYMER: __P51__
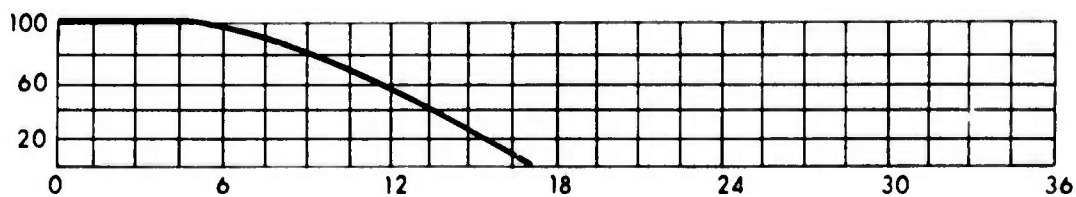
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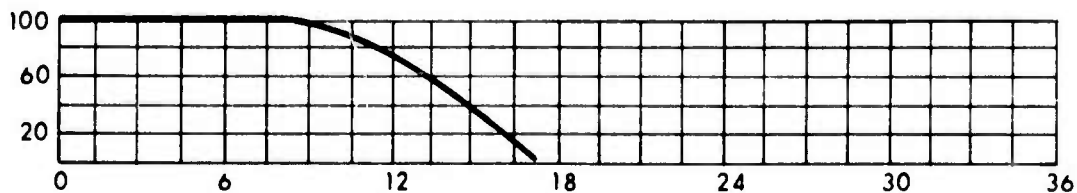
ORGANOMETALLIC POLYMER: __P53__

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ORGANOMETALLIC POLYMER: P54

ORGANOMETALLIC POLYMER: P56

ANTIFOULING PERFORMANCE, %
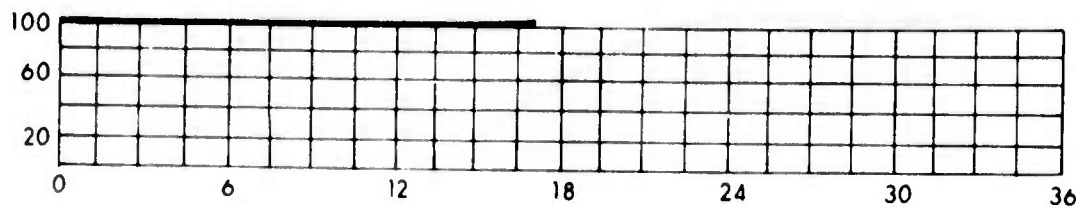
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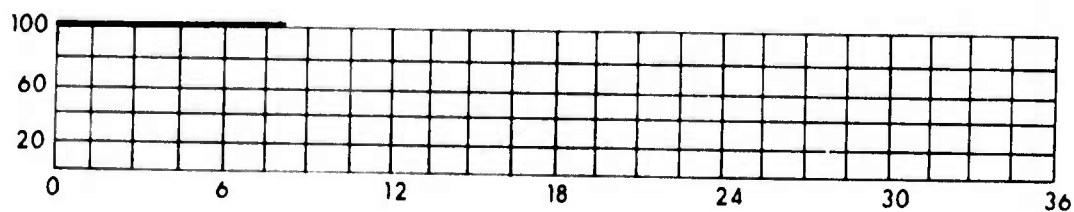
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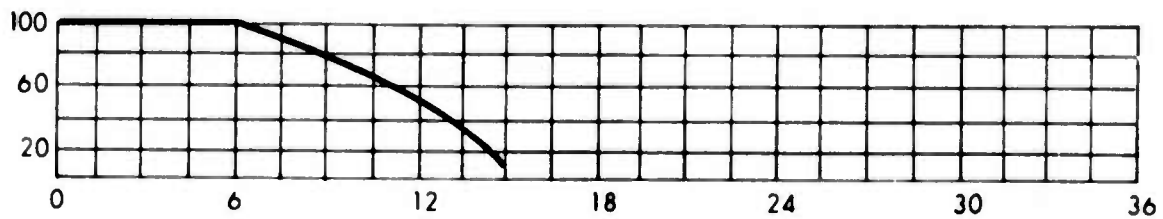
ORGANOMETALLIC POLYMER: BIOMET 410

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ORGANOMETALLIC POLYMER: 1020A
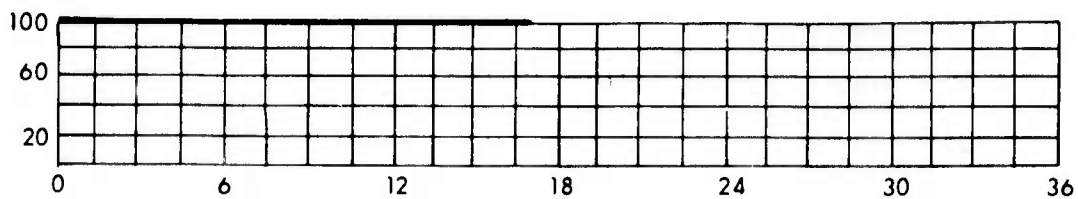
ORGANOMETALLIC POLYMER: OMP 1

ORGANOMETALLIC POLYMER: WS 41
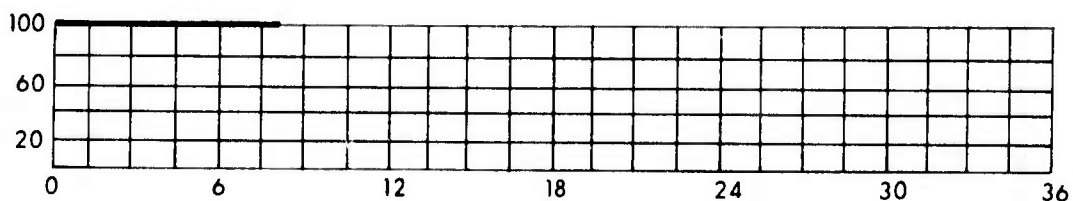
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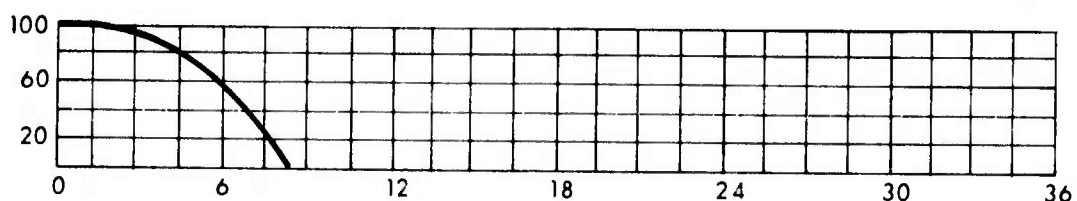
ORGANOMETALLIC POLYMER: WS 51

ANTIFOULING PERFORMANCE, %

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ORGANOMETALLIC POLYMER: __WS 52__

ORGANOMETALLIC POLYMER:_____

ORGANOMETALLIC POLYMER:_____
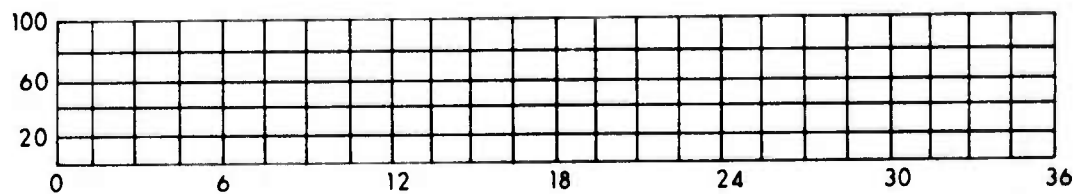
ORGANOMETALLIC POLYMER:_____

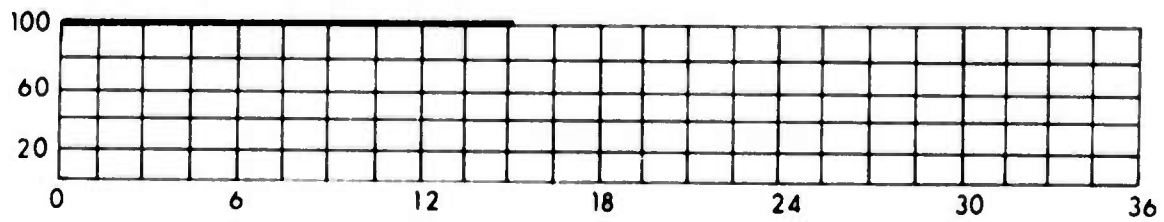ORGANOMETALLIC POLYMER:_____

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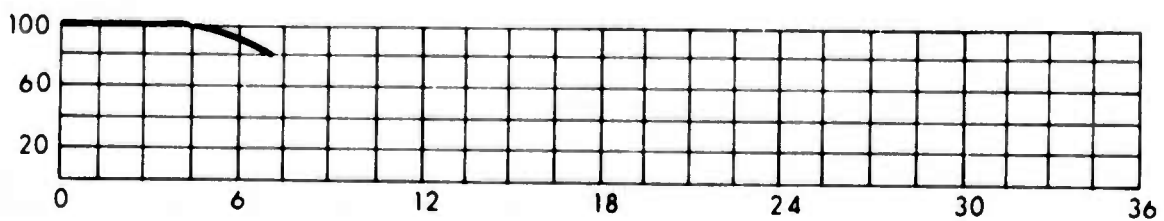
Pearl Harbor, Hawaii

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ORGANOMETALLIC POLYMER: ___37___

ORGANOMETALLIC POLYMER: ___P53___

ORGANOMETALLIC POLYMER: ___P54___
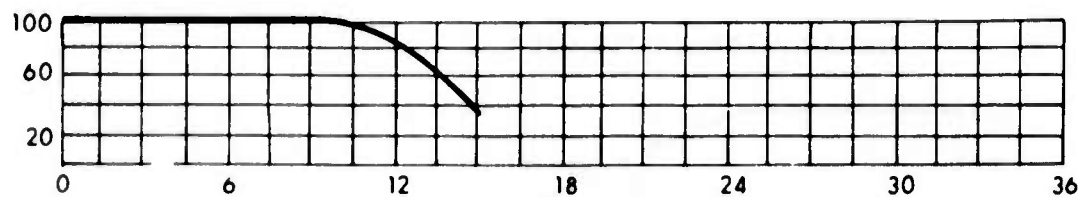

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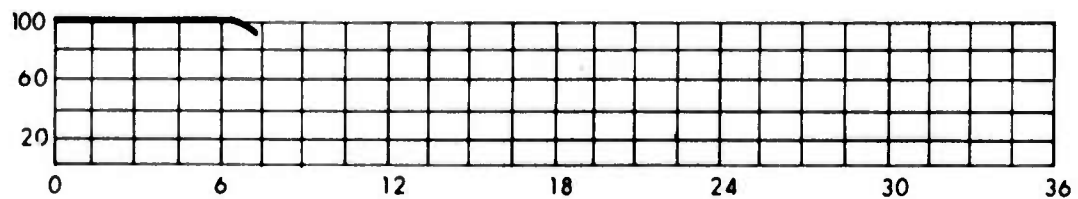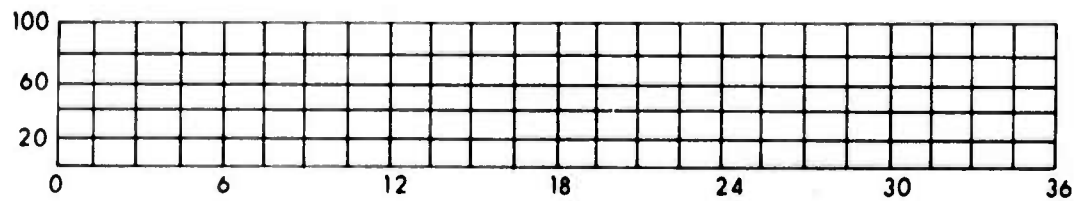

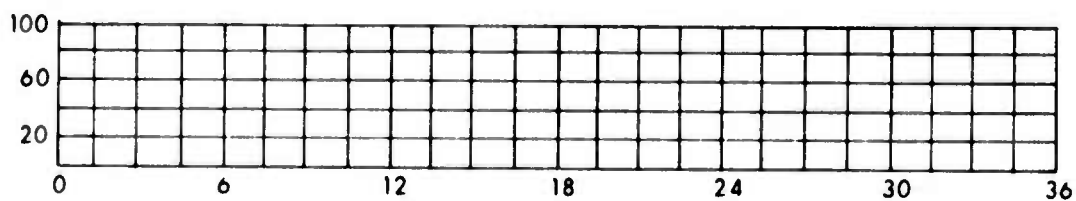ANTIFOULING PERFORMANCE, %

Miami Beach, Florida

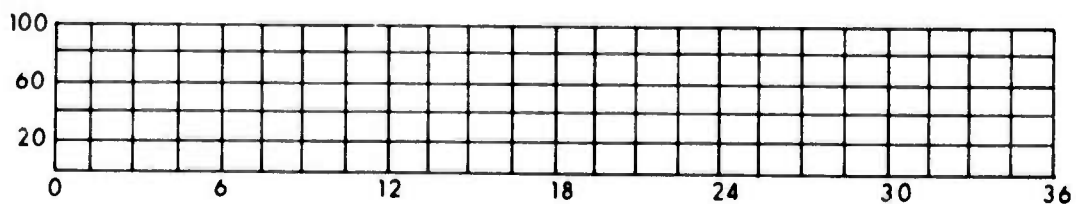ORGANOMETALLIC POLYMER: Formula 1020A

ORGANOMETALLIC PAINT: BIOMET 410

ORGANOMETALLIC POLYMER:_____

ORGANOMETALLIC POLYMER:_____

ORGANOMETALLIC POLYMER:_____

ANTIFOULING PERFORMANCE, %

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*Addressee.

4526, April 1975